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A copper–polyol complex: $[Na_2(C_2H_6O_2)_6][Cu(C_2H_4O_2)_2]$

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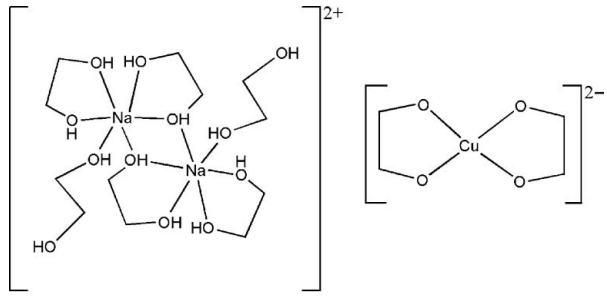
The ionic title complex, bis(μ-ethylene glycol)-$\kappa^3O,O':O'$;-$\kappa^3O:O,O'$-bis[(ethylene glycol-κ^2O,O')(ethylene glycol-κO)-sodium] bis(ethylene glycolato-κ^2O,O')copper(II), $[Na_2(C_2H_6O_2)_6][Cu(C_2H_4O_2)_2]$, was obtained from a basic solution of $CuCl_2$ in ethylene glycol and consists of discrete ions interconnected by O—H···O hydrogen bonds. This is the first example of a disodium–ethylene glycol complex cation cluster. The cation lies about an inversion center and the Cu^{II} atom of the anion lies on another independent inversion center.

Comment

There has been considerable interest in the coordination chemistry of metal ions in polyol media as this has relevance to our understanding of the reaction kinetics and solvent and ion exchange during reduction reactions. Several papers have investigated the mechanism of the polyol process by the study of kinetic data obtained by UV–visible and IR spectroscopy (Bonet *et al.*, 2000; Fievet *et al.*, 1988; Pasquarello *et al.*, 2001; Salmon *et al.*, 1992). From these data, metal glycolates have been postulated as possible intermediates. However, these studies do not provide definitive structural details for these species. We report here the structure of a Cu^{II} glycolate, $[Na_2(C_2H_6O_2)_6][Cu(C_2H_4O_2)_2]$, (I), which was obtained from a basic solution of $CuCl_2$ in ethylene glycol. A typical poylol reduction protocol was employed in which a basic ethylene glycol solution is used to reduce a metal such as Cu^{II} or Ni^{II} to the elemental form. The structure of the resulting complex consists of a di-chelate bis-ethylene glycolate dianion of Cu^{II} stabilized by ethylene-glycol-solvated Na ions. A survey of the literature reveals that only four examples of complexes containing the bis-ethylene glycolate Cu^{II} dianion have been crystallographically characterized (Habermann *et al.*, 1992; Love *et al.*, 1992; Pico *et al.*, 1997). These complexes contain Li^+, Ba^{2+} or Sr^{2+} as counter-ions. To the best of our knowledge, this is the first report of a crystal structure of an ethylene glycolate copper(II) dianion stabilized by ethylene-glycol-coordinated sodium counter-ions.



(I)

The molecular structure of (I) is illustrated in Fig. 1 and selected bond lengths are listed in Table 1. The anionic moiety consists of a bis-ethylene glycolate Cu^{II} dianion with the Cu atom on an inversion center, while the cation comprises two inversion-related Na ions complexed by chelating, bridging and monodentate ethylene glycol units.

The anion has square-planar coordination with fully deprotonated ethylene glycolate units which chelate the Cu^{2+} ion. The Cu1—O1 [1.9317 (13) Å] and Cu1—O2 [1.9252 (13) Å] distances fall between the previously reported Cu—O distances for $[Cu(C_2H_4O_2)]^{2-}$ (Habermann *et al.*, 1992; Love *et al.*, 1992; Pico *et al.*, 1997). A comparison of the Cu—O distances and angles from the previously reported structures of both ethylene glycolate and ethylene glycol copper complexes is given in Table 2. The Cu—O distances are consistently longer in the ethylene glycol complexes compared with the glycolate complexes. More significantly, the bite angle of the glycolate ligand is much larger than the protonated form by an average of 8°.

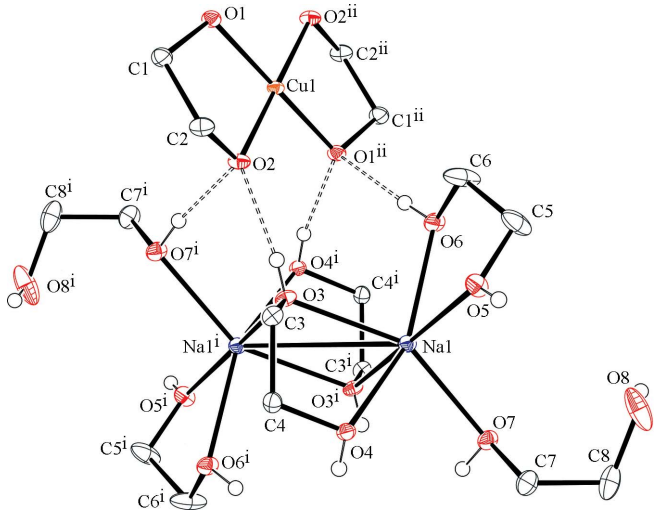


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Disordered atom O8*B* and methylene H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$.]

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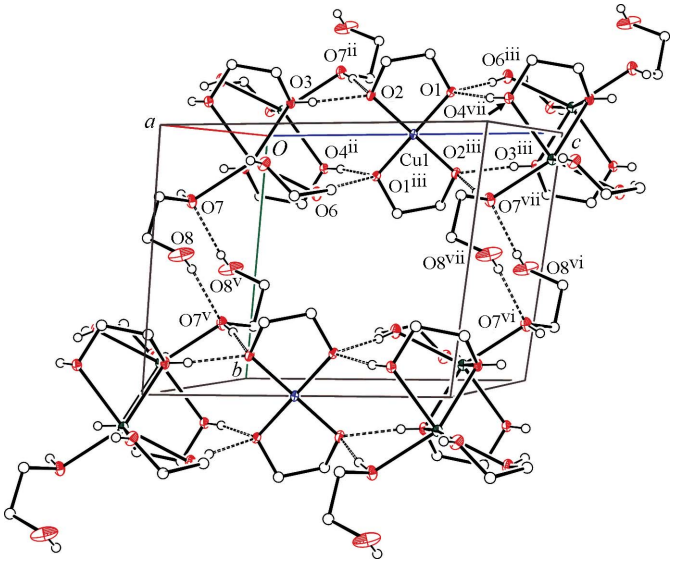

Figure 2
A packing diagram of (I), viewed approximately down the *a* axis, showing the hydrogen-bonding interactions between the anionic and cationic units. H atoms not involved in hydrogen bonding and disordered atom O8*B* have been omitted for clarity. [Symmetry codes: (ii) $-x, -y, -z$; (iii) $-x, -y, 1-z$; (v) $1-x, 1-y, -z$; (vi) $1-x, 1-y, 1-z$; (vii) $x, y, 1+z$.]

In the $[Na_2(C_2H_6O_2)_6]^{2+}$ cation, the unique Na ion is bound by two chelating ethylene glycols, one bridging O atom from an ethylene glycol that is chelating to the other inversion-related Na ion, and one monodentate ethylene glycol. The unique Na ion has a distorted octahedral coordination environment with Na—O distances in the range 2.3816 (16)–2.4545 (15) Å; the shortest distances come from the non-bridging chelating O atoms, *viz.* Na1—O6, and the longest distances arise from the bridging interaction of a chelating ethylene glycol, *viz.* Na1—O3($-x, -y, -z$). A search of the Cambridge Structural Database (CSD, Version 5.30 plus three updates; Allen, 2002) reveals only one previously reported structure with ethylene glycol bound to Na ions (CSD refcode: OBOBAI; Schubert *et al.*, 2000). In this structure, the Na ions are directly attached to the anionic portion of the structure through bridging ethylene glycol units and are therefore not part of an independent sodium–ethylene glycol cationic cluster as reported here.

The cations are linked by O5—H5···O4^{iv} and O8—H8···O7^{v} hydrogen bonds (see Table 3) to form sheets parallel to the (001) plane. Deprotonated atoms O1 and O2 of the anion are each hydrogen bonded to two different ethylene glycol O atoms of the cation, as shown in Fig. 1 with details in Table 3. The association of the two cations and anions *via* classical O—H···O hydrogen bonding (Table 3) results in a three-dimensional network with alternating layers of cations and anions down the *c* axis (Fig. 2).

The IR spectrum of (I) revealed weak C—O stretches at 1245 and 1218 cm^{-1} and weak *M*—O stretches at 541 and 606 cm^{-1}. These values are consistent with data obtained for the Cu–Sr structure $[Sr(C_2H_6O_2)_5][Cu(C_2H_4O_2)_2]$ (Pico *et al.*, 1997).

The synthesis of the title complex provides insight into complexes formed during the polyol process before metal reduction takes place. This study provides structural evidence of previously proposed metal glycolate formation during the polyol process.

Experimental

All reagents were used as received without further purification. For the preparation of (I), $CuCl_2(H_2O)_2$ (1 g, 5.87 mmol) and 4 equivalents of powdered NaOH (0.94 g, 23.46 mmol) were dissolved in ethylene glycol (25 ml). The solution was heated under reflux under a dry dinitrogen atmosphere and stirred magnetically (40 min); during this time the solution turned dark blue. The solution was then allowed to cool to room temperature. Crystals suitable for X-ray analysis were obtained from the solution by cooling to 248 K for 3 d in a sealed flask under nitrogen. The ethylene glycol was decanted off and the crystals were washed with diethyl ether (2 × 50 ml) and hexane (2 × 50 ml). Unoptimized yield: 2.4 g, 68% (based on Cu); m.p. 386–388 K (decomposition). FT–IR [cm^{-1}, ATR (attenuated total reflectance)]: ν(CO) 1245 (*w*), 1218 (*w*); ν(*M*O) 541 (*w*), 529 (*w*).

The crystals are deliquescent and readily form droplets within an hour of sitting in air. The crystals are insoluble in common organic solvents but dissolve readily with decomposition in alcohols and water. Attempts to isolate a nickel intermediate from an analogous reaction using $NiCl_2(H_2O)_6$ were unsuccessful.

Crystal data

$[Na_2(C_2H_6O_2)_6][Cu(C_2H_4O_2)_2]$
M_r = 602.03
Triclinic, $P\overline{1}$
a = 8.7666 (12) Å
b = 9.5089 (13) Å
c = 9.7804 (13) Å
α = 99.152 (4)°
β = 101.983 (4)°
γ = 113.910 (4)°
V = 701.61 (16) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.88 mm^{-1}
T = 100 K
0.09 × 0.09 × 0.08 mm

Data collection

Rigaku AFC-12 with Saturn 724+CCD diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.573, T_{max} = 0.9
7103 measured reflections
3177 independent reflections
2863 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.080
S = 1.07
3177 reflections
190 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

The nonchelating O atom from an ethylene glycol ligand bound to sodium was disordered over two positions, *viz.* O8 and O8*B*, whose occupancy factors were refined and then fixed at 0.911 and 0.089, respectively. The C8—O8 and C8—O8*B* distances were restrained to be equivalent. All methylene H-atom positions were calculated using the appropriate riding model, with U_{iso}(H) = 1.2U_{eq}(parent atom) and C—H = 0.99 Å. The hydroxy H atoms were located in a difference Fourier map and refined freely.

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

Table 1
Selected bond lengths (Å).

Na1—O6	2.3816 (16)	Na1—O5	2.4052 (16)
Na1—O7	2.3858 (16)	Na1—O4	2.4453 (15)
Na1—O3	2.3945 (16)	Na1—O3^{i}	2.4545 (15)

Symmetry code: (i) $-x, -y, -z$.

Table 2
Comparison of known copper ethylene glycolate and ethylene glycol complexes.

Complex	CSD refcode	Average Cu—O (Å)	Bite angle of $C_2H_4O_2$ (°)
$Na_2Cu(C_2H_6O_2)_6(C_2H_4O_2)_2$	This work	1.929 (3)	87.11 (5)
$BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$	PAHFEJ[a]	1.921 (4)	88.6 (3)
$BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$	PAHFAF[a]	1.923 (5)	86.65 (15)
$Li_2Cu_2(C_2H_4O_2)_2$	VOWKAT[b]	1.931 (13)	87.22 (6)
$CuCl_2(C_2H_6O_2)_2$	CETDCU10[c]	1.978 (19)	79.1 (1)
$CuCl_2(C_2H_6O_2)_2\ H_2O$	GLYCUH[c]	1.986 (18)	79.9 (1)
$Cu(C_2H_6O_2)_3(SO_4)$	ETDOCU[d]	2.10 (10)	79.2 (10)

References: (*a*) Pico *et al.* (1997); (*b*) Habermann *et al.* (1992); (*c*) Antti (1976); (*d*) Antti *et al.* (1972).

Table 3
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O1^{ii}	0.75 (3)	1.93 (3)	2.683 (2)	175 (3)
O4—H4···O1^{iii}	0.74 (3)	1.89 (3)	2.6153 (19)	168 (3)
O5—H5···O4^{iv}	0.75 (3)	2.05 (3)	2.779 (2)	164 (3)
O7—H7···O2^{i}	0.81 (3)	1.81 (3)	2.612 (2)	171 (3)
O3—H3···O2	0.72 (3)	1.94 (3)	2.6566 (19)	172 (3)
O8—H8···O7^{v}	0.69 (3)	2.14 (3)	2.815 (3)	167 (4)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, -z+1$; (iii) $x, y, z-1$; (iv) $-x+1, -y, -z$; (v) $-x+1, -y+1, -z$.

structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3156). Services for accessing these data are described at the back of the journal.

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